

Conference Paper

Composition, Properties and Using Fields of Product of Phosphogypsum Recycling

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Abstract

Nowadays about 200 million tons of phosphogypsum (PG) have been stored in the dumps of the chemical industry and non-ferrous metallurgy of Russia which pollutes the environment. This waste contains up to 98 % of two-water gypsum and impurities including rare earth metals (REM) in an amount of up to 0.5 % preventing its use in the production of building materials. A complex technology of FG recycling including extraction of REM, neutralization and dehydration of the pulp for using in the production of gypsum binders and Portland cement. Results of determination of density, grain, chemical and mineral compositions and structure of the product of recycling of FG of the "Sredneuralsky copper smelting plant" are presented. After the REM extraction, the PG is a loose lumpy mass with moisture content of 28–32 % which contains about 10 % of particles larger than 40 mm and not more than 60 % of particles less than 10 mm, it has a true density of 2.26 g/cm³, pH of aqueous extract is 5.95. It has the following chemical composition, mass. %: 0.87 SiO₂; 0.93 Al₂O₃; 0.20 Fe₂O₃; 31.00 CaO; 0.034 MgO; 44.27 SO₃; 0.10 K₂O; 0.42 Na₂O; 0.45 P₂O_{5(general)}; 20.73 of mass loss of ignition. The mineral composition of the PG processing product is represented by two-water gypsum and a slight amount of quartz. The possibility of using gypsum-containing waste in the production of gypsum binders and cement is considered. The effect of temperature and duration of firing, the dispersion, the type and quantity of chemical and mineral admixtures on physical and mechanical properties of gypsum binder, the influence of the type and amount of mineral additive on pelletizing and physic-mechanical properties of the granulated and pressed PG and its effects on setting time and strength of Portland cement are represented. It is recommended to use PG to obtain low-temperature and composite gypsum binders, regulation of Portland cement setting after extraction of REM.

Keywords: phosphogypsum, recycling, composition, properties, technology, gypsum binder, Portland cement

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1. Introduction

Phosphogypsum is a large-scale waste of mineral fertilizers production. Currently, only in the dumps of industrial enterprises of Russia about 200 million tons of phosphogypsum (PG) have been accumulated and the volume of its storage increases by 10–15 million



tons annually. PG dumps occupy large land areas, they pollute the air and soil, get into the aquifer with harmful soluble compounds of fluorine, phosphorus and other impurities.

Phosphogypsum contains from 80 to 98 % of dihydrous gypsum and can be classified as gypsum raw materials. However, PG contains a significant quantity of impurities that are soluble and slightly soluble in water and can significantly affect the quality of gypsum binders and construction products. Thus, with an increase amount of phosphates and fluorides in PG temperature of dehydration $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to semi-aquatic calcium sulfate is reduced from 140 to 110 °C. The high content of phosphoric acid and phosphates slows down the hydration process, setting, hardening of gypsum binders and cements and reduces the strength of artificial stone [1–3]. Rare earth metals (REM) such as strontium and cerium in a quantity up to 0.5 % in PG also slow hardening of gypsum binders. Dumps of the largest Russian enterprises contain about 100 000 tons of rare earth metals in the PG. Their extraction can significantly change the situation with rare-earth elements not only in Russian but also in the world economy.

The main raw materials for production of gypsum materials and products are natural gypsum stone and anhydrite, and gypsum-containing wastes of several industries (phosphogypsum, fluorine hydrate, titanium gypsum, boron gypsum, etc.). The consumption of natural gypsum is more than 110 million tons per year in the world. However, the aggregate state, composition and properties of PG differ significantly from natural gypsum raw materials that complicates its industrial recycling into construction products. High humidity and content of undesirable impurities require additional technological operations namely drying and neutralization of PG. To obtain PG with a composition and properties similar to natural gypsum it is necessary to decompose the phosphoric raw materials according to the methods proposed by ‘Nissan Chemical’ (Japan) and ‘Central-Prayon’ (France). These methods allow to recycle PG into construction materials using cost-effective and technically efficient technologies [4].

Another possible way of PG conditioning can be the technology of extraction of REM by leaching which provides formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as a by-product that is ‘purified’ from water-soluble substances and rare earth compounds. Complex technology of PG recycling including extraction of REM, neutralizing of the pulp with use of lime and dewatering, obtaining of a product suitable for use in the production of gypsum binders and Portland cement has been developed by the specialists of the Ural Federal University [5, 6]. In general REM extraction technology includes sorption leaching, REM desorption from ion exchanger, conversion of the ion exchanger, REM deposition from solution in the form of carbonates, chalk deposition from the regenerating solution before returning. The chemical composition of PG enriched by this method is close to

a natural gypsum stone that expands the using ways and simplifies the technology of its processing into construction materials.

2. Results and Discussion

The technology of REM extraction from the dump phosphogypsum of JSC “Sredneuralsky copper melting plant” (Sverdlovsk region) was fulfilled at pilot plant. Within two months more than 40 tons of PG was recycled and more than 100 kg of collective concentrate with a purity of 97–99 % according REM oxides was obtained. After the REM extraction the product of PG recycling was a loose lumpy mass with an average moisture content of 31 % which has a light gray color, in dry state – white one and the grain composition is following, %: more than 40 mm – 8.4; 20–40 mm – 16.8; 10–20 mm – 17.5; less than 10 mm – 57.4. The maximum size of the piece is 100 mm. The true density of PG is 2.26 g/cm³, the bulk density in the dry state is 630 kg/m³. The specific surface of the dry powder is 321 m²/kg, grain composition of the powder is following, %: 0.082–0.125 mm – 4.21; 0.060–0.082 – 20.40; 0.040–0.060 – 26.81; 0.019–0.040 – 14.90; 0.010–0.019 – 11.37; 0.004–0.010 – 13.29; 0.001–0.004 – 7.56; less than 0.001 – 1.46; pH of the aqueous extract is 5.95. Product of phosphogypsum recycling has the following chemical composition, %: 20.73 of mass loss of ignition; 0.87 SiO₂; 0.93 Al₂O₃; 0.20 Fe₂O₃; 31.00 CaO; 0.034 MgO; 44.27 SO₃; 0.10 K₂O; 0.42 Na₂O; 0.45 P₂O_{5(general)}; 0.016 P₂O_{5(solub)}; 0.009 PbO; 0.003 CuO; 0.001 ZnO; 0.983 other.

According to X-ray phase analysis product of PG recycling consist of calcium sulfate dihydrate and a small amount of quartz.

As to differential thermal analysis it was established that the dehydration process of PG begins at a 125 °C and ends at 273 °C, it has a clearly noticeable double endothermic effect of dehydration of Calcium Sulfate Dihydrate. The first endothermic effect with a maximum point at 180.8 °C characterizes the formation of Calcium sulfate hemihydrate, and the second one with the maximum point at of 205.6 °C is associated with the formation of soluble anhydrite. The exothermic effect at 444 °C is due to the polymorphic transition of soluble anhydrite to insoluble. The content of Calcium sulfate hemihydrate in the product of PG recycling was calculated using the quantity of mass loss and was equal to 94.6 % (for dry substance). According to this index PG corresponds to 1 grade of gypsum raw materials (Russian Standard no. 4013–82).

It was known that product of phosphogypsum recycling consists of 98–99 % calcium sulfate dihydrate crystals having prismatic and tabular form with clear crystallographic outlines (see Figure 1). Crystals are weakly connected with each other, the destruction of their aggregates goes on the points of contact of gypsum grains and is accompanied by

only partial splitting of the crystals themselves during the hydro-mechanical treatment. Their faceting is fully referred to penicilina view of the symmetry of the monoclinic system.

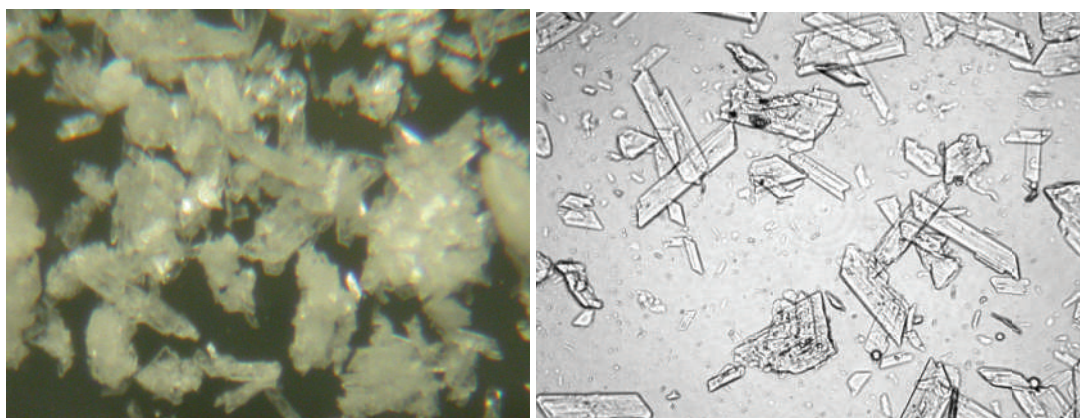


Figure 1: Structure of the product of phosphogypsum recycling under binocular microscope (a) and a passing light microscope (b) (authors' work).

The size of gypsum crystals varies mostly from 20×6 to 350×110 μm with predominance of particles with a length of $40\text{--}60$ μm and a thickness of $15\text{--}20$ μm . As this fact it can be concluded that the growth rate of dihydrate gypsum during producing in the reactor PG differ in crystallographic directions by 5–6 times. The refractive indices of gypsum crystals are normal and equal $n_g = 1.520$, $n_p = 1.529$. Thus, in comparison with the initial PG the product of its recycling is characterized by lower acidity and content of harmful impurities, greater dispersion and heterogeneity in the size of crystals of double–water gypsum. The absence of fluorides in it will favorably affect the subsequent recycling of this product into gypsum binders and cements.

In order to study the possibility of obtaining a gypsum binder from the product of phosphogypsum recycling the optimal temperature–time conditions of heat treatment was determined. The effect of dispersion, type and quantity of chemical and mineral additives on the physical and mechanical properties of calcium sulfate β –semihydrate was investigated. To obtain a grade gypsum binder of at least G–5, it is recommended β –semihydrate to be ground to a specific surface of $800\text{--}1000$ m^2/kg , and with the addition of 0.2–0.3 % superplasticizer Melflux 4930F – up to $700\text{--}800$ m^2/kg . High heat dissipation during hydration indicates a greater activity of phosphogypsum binder compared to the binder from natural raw materials. The value of the hydration heat depends on the crystal specific surface and size and the nature of the semihydrate crystallinity, as well as on the characteristics of raw materials and the features of their heat treatment [7]. The higher the specific surface, the smaller the crystals size and the greater the thermal pressure of the semihydrate formation, the higher the heat value of its hydration and the reactivity of the gypsum binder.

A pilot batch of phosphogypsum binder was produced, the properties of which meet the requirements of Russian Standard no. 125–79 (grade G–7 BIII which is mean 7 MPa, normally hardening, fine grinding). The composition of the composite gypsum binder G–10 obtained by joint milling of 90 % β –semihydrate from PG, 10 % limestone and 0.2–0.3 % superplasticizer was developed. PG pelletizing contributes to its wider use in cement production [8, 9]. The influence of the type and amount of mineral additive on granularity and physico-mechanical properties of the granulated and pressed product of PG recycling. To obtain an artificial gypsum stone the product of PG recycling is recommended granulate with 20-30 % of the burned PG additive which provides the formation of granules with strength sufficient for transportation and subsequent processing. When storing granulated PG in water alkaline effluents are not formed, its strength is not significantly reduced; according to the content of double-water gypsum it is referred to gypsum raw materials of 1 grade according to Russian Standard no. 4013–82. Physico–mechanical properties of Portland cement with the addition of granulated artificial stone from PG meet the requirements of Russian Standard no. 31108–2016.

3. Conclusion

As a result of the composition research, structure and properties of the product of the PG recycling after the extraction of REM were determined, the possibility of its use for producing of low–temperature and composite gypsum binders and as a gypsum–containing additive to regulate the setting of Portland cement was established.

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